

Estimating Potential Impacts of Chemical Contaminants in Stormwater on Sediment and Fish in Portland Harbor (Lower Willamette River, Oregon)

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This draft was updated on 6/12 by KT (per Bruce's direction) to reflect revised model outputs due to an update to Henry's Law constant, and an updated calculation of observed fish tissue concentrations. These changes have been tracked in the document.

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1. INTRODUCTION

The Willamette River Basin covers approximately 32,000 km² of land between the crests of the Cascade and Coast Ranges in northwestern Oregon, USA (Ulrich and Wentz 1999). Its drainage system is dominated by the Willamette River and its 13 major tributaries (Figure 1). The Willamette River is one of only fourteen American Heritage rivers, has the thirteenth largest streamflow in the U.S., and yields more runoff per square mile than any other large river in the U.S. (Ulrich and Wentz 1999). It arises in two forks, the Coast and the Middle, which flow northward to form the mainstem near Eugene, which then continues northward for approximately 187 river miles (RM) to its confluence with the Columbia River at Portland, Oregon (Laenen and Risley 1997; Woodward et al. 1998). Oregon's three largest urban areas, the cities of Portland, Salem, and Eugene, border the river (Altman et al. 1997). The approximately 2 million people (≈70 percent of the state's population) who live or work in the Basin depend on the river for many resources, but also contribute to potential pollution problems associated with many residential, municipal, industrial, or agricultural activities.

The lower reach of the Willamette River, which extends from its confluence with the Columbia River to Willamette Falls at approximately RM 26.5 is wide, shallow, slow moving, and tidally influenced as far upstream as RM 15. A federal navigation channel, with an authorized depth of -40 feet MLLW, extends from the confluence to RM 11.6. This channel deepening, along with stabilization of the channel banks, has created a stable channel in this portion of the lower river. Between the confluence and RM 11.6 is a highly industrialized area, known as Portland Harbor ("Harbor"), where numerous industrial activities, such as an oil gasification plant, ship repair facilities, agricultural chemical manufacturing, rail car construction, wood treating facilities, and port activities, have occurred or are occurring (Figure 1). A joint Oregon Department of Environmental Quality (ODEQ) - U.S. Environmental Protection Agency (USEPA) study of sediment in the Harbor, completed in 1998, found it to be contaminated with polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides (primarily DDT and its metabolites), herbicides, dioxins/furans, and metals. These findings lead to the reach between RM 3.5 and 9.5 being designated a National Priorities List ("Superfund") site in December, 2000; this reach is referred to as the Initial Study Area (ISA). In September, 2001, USEPA signed an administrative consent order for the completion of a remedial investigation and feasibility study (RI/FS) within the ISA (LWG 2004). Subsequent work reported elevated levels of organic and inorganic contaminants in the tissues of fish resident within the ISA (Sethajintanin and Anderson 2006; USEPA 2006). Because recreational, sport, and

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subsistence fishing are extremely popular in the lower river and resident species are fished throughout the year, the presence of chemical contaminants in fish has raised concerns about human health impacts from consumption of fish caught within the ISA.

Chemical contaminants detected in the ISA may come from several sources, including upstream (i.e., “background” loads with respect to the ISA), in-river (i.e., from sediment contaminated by past (legacy) or current (continual or episodic) releases), atmospheric deposition of aerosol or gas phase contaminants directly to surface water, or stormwater discharges (which includes a contribution from atmospheric deposition to land). Because over 250 private and public stormwater outfalls, including storm drains and combined sewer overflows, enter the ISA, stormwater runoff is considered a potentially significant mechanism for transporting chemical contaminants to the ISA from the highly urbanized and industrialized upland areas within its watershed. Unfortunately, sufficient, reliable, and quantitative data on which to base an estimate of contaminant contributions from stormwater to sediment and fish tissue are not presently available. This data gap could slow the design and conduct of cost-effective stormwater data collection efforts, as well as hamper discussions of future stormwater control and management strategies and policies. It was decided, therefore, to address this data gap in the short-term with two models: one that estimates contaminant transport and fate within the ISA and another that uses a Harbor-specific aquatic food web to estimate contaminant levels in resident fish. Modeling was a cost-effective means of providing environmental managers with initial quantitative insights into how stormwater discharges, as well as any stormwater control and management strategies, could affect chemical levels in sediment and biota within the ISA. Here these models are simply tools for summarizing the existing state of knowledge, synthesizing information on specific chemicals in the Harbor, predicting the response of chemical concentrations to management actions and natural processes, identifying and prioritizing data gaps, and communicating results. In the longer-term, it is anticipated that empirical stormwater data will become available, allowing for a more accurate appraisal of the total load to the river that is attributable to stormwater.

The purpose of this study is to explore, through modeling, seven scenarios related to the impact of various sources on contaminant levels in sediment and fish tissue. First, how could upstream sources alone impact contaminant levels in fish, assuming “clean” (hypothetically zero chemical concentration) sediment and no other sources? Second, how could atmospheric deposition (to water and conveyed from land by stormwater) impact contaminant levels in sediment and fish, assuming “clean” (hypothetically zero chemical concentration) sediment and no other sources? Third, how could upstream sources and atmospheric deposition impact

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contaminant levels in sediment and fish, assuming “clean” (hypothetically zero chemical concentration) sediment and no other sources? Fourth, with respect to development of a general stormwater permit for the ISA, what is the maximum contaminant load in stormwater that would not cause an exceedance of an acceptable sediment level, assuming continuing upstream and atmospheric sources and clean sediment? Fifth, with respect to maintaining fishing as a beneficial use in the ISA, what is the maximum contaminant load in stormwater that would not cause an exceedance of a fish consumption advisory, assuming continuing upstream and atmospheric sources and clean sediment? Sixth, how do currently observed sediment concentrations impact contaminant levels in fish, assuming continuing upstream and atmospheric sources but no land-based stormwater sources? Seventh, with respect to establishing a reasonable cleanup goal, how would sediment concentrations at the sediment screening level value (SLV) impact contaminant levels in fish, assuming continuing upstream and atmospheric sources but no land-based stormwater sources? Results from Scenarios 1, 2, 3, and 6 were combined to provide an estimate of the contaminant levels in fish tissue attributable to upstream, atmospheric, stormwater, and or sediment contamination.

2. METHODS

2.1. CONTAMINANTS OF INTEREST

Although a number of persistent, hydrophobic, organic chemicals are present in the Harbor, polychlorinated biphenyls (PCBs) are the primary risk drivers. PCBs are a class of 209 individual compounds (or congeners) that vary widely in their chemical and toxicological properties. The degree of chlorination influences transport and fate behavior, in that congeners with fewer chlorines are more volatile, more water soluble, and more reactive than more highly chlorinated congeners. However, for logistical, data availability, and toxicological reasons, it is neither possible or necessary to model all 209 congeners. Of the 209, a dozen are now considered to be “dioxin-like” because of their toxicity and certain features of their structure which make them similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) (Van den Berg et al. 2005). The four congeners considered in this study were selected primarily on the basis of their toxicity relative to 2378-TCDD, their occurrence in various media (sediment, water, air, tissue) within the Harbor and the Basin, and their documented presence in stormwater at other localities. These include three non-*ortho* substituted (coplanar) congeners (3,3',4,4'-tetrachlorobiphenyl (PCB-077), 3,3',4,4',5-pentachlorobiphenyl (PCB-126), 3,3',4,4',5,5'-hexachlorobiphenyl (PCB-169)) and one mono-*ortho*-substituted congener (2,3'4,4'5-

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pentachlorobiphenyl (PCB-118)). Although it was not a key factor in their selection, each does represent a different degree of chlorine substitution, which may lead to important differences in their environmental transport and fate. Aroclors (commercial mixtures of various congeners) were not included because they are not physicochemically distinct and can undergo composition changes in the environment after release.

The three non-*ortho* substituted congeners are the most toxic (relative to 2378-TCDD) and thus of greatest concern with regard to exposure of humans and wildlife that eat fish from the Harbor. Although PCB-118 is not as toxic as the three non-*ortho* substituted congeners, it is typically present in the Harbor and Basin environments in much greater mass, making it a significant contributor to total toxicity. For example, in smallmouth bass tissue taken from the Harbor, it is the second greatest contributor, after PCB-126, to the potential for dioxin-like toxicity. PCB-118 has been found to be the largest single contributor to total 2,3,7,8-TCDD equivalents in human serum and adipose tissue from the United States, Japan and Sweden (Patterson et al. 1994). Although the coplanar congeners were not detected in surface water or fish tissue collected within and near the Harbor, PCB-118 was found to be the third most abundant congener in fish tissue and clearly present in surface water (Sethajintanin et al. 2004; Sethajintanin and Anderson 2006). Because of their physicochemical similarities, the environmental fate of PCB-118 is a good indicator for that of PCB-126, which is typically found at much lower, and thus more challenging to quantify, concentrations (Davis 2003, 2004). In sampling conducted in Oregon as part of the National Dioxin Air Monitoring Network (NDAMN) program, all three coplanar congeners were detected in ambient air (particle and vapor combined) in the Willamette Basin; PCB-118 was the congener present at the highest concentration (Cleverly et al. 2007). PCB-118 is also the most abundant ($\approx 13\%$) by weight in Aroclor 1254 (Frame et al. 1996). In other localities, PCB-118 has been found to be prominent in urban stormwater (Rossi et al. 2004), one of the congeners with the highest concentrations in water pollution control plant (WPCP) discharges (Durell and Lizotte 1998), and a significant portion of the total PCB load in street dust that may ultimately become a component of stormwater runoff (Loganathan et al. 1997). It has also been reported in rainwater (both vapor and aerosol phases), but is not among the congeners present at the highest concentrations (Duinker & Bouchertall 1989; Mandalakis & Stephanou 2004). Key physicochemical and toxicological properties of the congeners being modeled are summarized in Table 1.

2.2. MODEL SYSTEM

The impact of episodic and transient releases of chemicals conveyed by stormwater may be

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more “memorable” in sediment and fish tissue because the time constant of response is longer in these media than in surface water. It is thus important to provide simultaneous, time-dependent estimates of chemical concentrations in all media (sediment, surface water, and tissues of aquatic organisms) that may be affected by stormwater discharges. The overall model design responds to this specification by linking a mass balance transport and fate model to a Harbor-specific food web biomagnification model. These rate constant models assess the distribution of persistent organic chemicals in abiotic and biotic media primarily as a function of the octanol-water partition coefficient. Similar models have been successfully applied to a variety of chemical issues in lakes, rivers, and marine environments (Gobas et al. 1995, 1998; Diamond et al. 1996; Mackay et al. 1994; Mackay and Hickie 2000; Davis 2003, 2004; MOE 2001). Outputs from the transport and fate model are fed (Figure 2) to a Harbor-specific food web biomagnification model to produce estimates of chemical concentrations in tissues of various aquatic biota. These dynamic non-steady-state models are implemented in Visual Basic® using forward Euler integration, allowing changes in sediment, water, and tissue concentrations to be tracked both over time and at steady-state (Gobas et al 1998; Mackay 2001). Because of the half-life of the persistent organic chemicals being modeled, these models are designed to simulate conditions daily for up to 20 years (7,300 days). The transport and fate model uses a Δt of 0.01 to meet the Courant criterion, awhile the food web model uses a Δt of 1.0 for consistency with its rate constants.

2.3. MODEL DOMAIN AND STRUCTURE

The model domain extends from river mile (RM) 12.0 to RM 1.8 along the mainstem of the Willamette River (Figure 1). This domain is divided into 36 rectangular segments (Figure 3). Placement of these divisions was informed by the location of sediment management units and knowledge of areas favoring erosion or deposition, as well as of physical features such as habitat areas, grain size, modeled bottom shear forces, river bathymetry and the presence of the shipping channel. The Shipyard Lagoon is an additional segment (Segment 37); an embayment connected to the main river at Segment 15. Parameters that would affect total flows and the amount of flow diverted down Multnomah Channel include relative stage of the tides in St. Helens and Portland, flow in the Columbia River, and Willamette River flow into the Harbor. It was assumed, based on limited data, that 90 percent of the flow from segment 31 and 50 percent from segment 32 is diverted from the main river into Multnomah Channel. There is also a significant change in hydraulic cross section at approximately RM 3.0, where the Multnomah Channel connects with the mainstem (Laenen and Risley, 1997). There are 33

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segments located upstream (the “upper” harbor) and 3 segments located downstream (the “lower” harbor) of this change in hydraulic cross-section.

Each segment consists of a water column and an active sediment compartment (Figure 4). These compartments are assumed to be homogeneously mixed. Harbor sediments are conceptually divided into active and buried sediment layers. The active sediment layer is the mass of sediment that is actively exchanging chemicals with the water column and Harbor food webs. The depth of this layer is dependent on bioturbation and mixing driven by tides and river flows. The buried sediment layer consists of any Harbor sediment that is too deep to exchange chemicals with the active sediment layer and water column. The accessible (or active layer) represents those bottom sediments that participate in the exchange of chemical between the water and the sediments. The inaccessible (buried) layer is a sink to the model. Large removal rates of sediment-bound chemical during periods of net sediment erosion are achieved by parameterizing with the high suspended sediment concentrations typically observed under these conditions. The river water is assumed to be well-mixed or homogeneous in composition, thus once the chemical has entered the river its source becomes immaterial (i.e., the chemical “forgets” its origin). This well-mixed assumption is a key simplification. Similarly the bottom sediment is assumed to be a single well-mixed layer of defined depth, beneath which are buried, inaccessible sediments. This is another key simplification. These simplifications are not necessarily a correct representation of sediment dynamics, but are acceptable from a chemical fate perspective.

2.4. TRANSPORT AND FATE MODEL

Algorithms and variables for the transport and fate model, with the exception of the fluxes noted below, are as described in Davis (2003, 2004). Model input variables, their values, and sources are summarized in Table 2. Spatial relationships and values for the key physical variables for each segment are summarized in Figure 3. It is assumed that values for the physical variables in the model (e.g., segment width, water velocity, solids settling rate, etc.) remain constant regardless of the chemical being modeled. In other words, different chemicals could not experience physically different model rivers.

The water and sediment compartments in each segment are acted upon by the same number and type of chemical input and output fluxes (Figure 4). Inputs to the water column include resuspension of sorbed chemicals from sediment (FSW1), diffusion of dissolved chemicals from sediment (FSW2), and downstream, lateral, and tidally-driven fluxes (FQD, FQX, FQT). Loads to the water column from sources external to the model domain include

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those from stormwater (SWL), upstream (USL), and downstream (DSL) sources, as well as deposition direct from the atmosphere to water (FAW); SWL combines contributions from land-based sources with deposition from the air to land (FAL) within the ISA watershed. Re-volatilization of contaminants from land to air (FAL) is noted but not quantified in the model. Outputs from the water compartment include volatilization to the atmosphere (FWA), outflow of particulate and dissolved chemicals downstream or laterally (FQD, FQX), deposition of particle-bound chemicals to the active sediment layer (FWS1), diffusion of dissolved chemicals to the active sediment layer (FWS2), and degradation of particulate and dissolved chemicals (FRW). Inputs to the active sediment layer include deposition of particle-bound chemicals from the water column (FWS1) and diffusion of dissolved chemicals from the water column (FWS2). Output fluxes from the active sediment layer include resuspension of sorbed chemicals to the water column (FSW1), diffusion of dissolved chemicals to the water column (FSW2), burial of sorbed chemicals as inaccessible deep sediment (FB), and degradation of sorbed and dissolved chemicals in sediment (FRS). Mass movement between segments occurs through movement of water and of particles suspended in water; bed load transport is not simulated. Three fluxes control such movement between segments: (1) downstream flow of the mainstem Willamette River (FQD), (2) tidally-driven flows between segments up- and downstream of one another (FQT), and (3) lateral flows between adjacent segments (FQX) (Figure 5). Neither tidal or lateral flows occur unless there is a concentration gradient between their respective segments.

2.4.1. DOWNSTREAM FLUX ESTIMATION AND APPORTIONMENT

Because the model divides the width of the river into three parallel segments, the total downstream flow, velocity, and hydraulic area of the river must be apportioned to each segment (Figure 5). Apportionment begins by estimating the total hydraulic cross-section area as a function of river stage, based on a regression relationship developed from USGS data collected at RM 12.8, then velocity as a function of cross-section area and flow.

$$FQD = ((QA \cdot CF_{LD}) / (CF_{LM} \cdot VW)) \cdot WAT \quad (1)$$

$$QA = (Q / XSA \cdot UAF) \cdot XSA \cdot XAF \quad (2)$$

$$XAF = WID / WID_T \quad (3)$$

$$VW = LEN \cdot XSA \cdot CF_{FM} \quad (4)$$

where: FQD = Flux due to downstream flow (kg d⁻¹), WAT = Chemical mass in the water reservoir (kg); QA = Apportioned flow of daily mean flow (ft³ s⁻¹), CF_{LD} = Conversion factor (2446575.5808 L ft⁻³ • s d⁻¹), CF_{LM} = Conversion factor (1000 L m⁻³), CF_{FM} = Conversion factor

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($0.0929 \text{ m}^2 \text{ ft}^{-2}$), WID_T = Width of river (i.e., three adjacent segments) (m), VW = Water volume (m^3), XAF = Channel hydraulic cross section area apportionment factor (unitless), and XSA = Channel hydraulic cross section area (ft^2).

The mean of daily mean water flow for a given day (Q) were obtained from USGS gage 14211720 (Willamette River at Portland, OR; RM 12.8) for the period 1972 - 2004. Although segments have differing lengths, initial runs indicated that model performance would not be compromised if the width (WID) of all side segments was the same (10 m), as well as that for all center segments (380 m in upper harbor, 480 m in the lower harbor). The width of side segments was selected to encompass the more biologically relevant areas of the river.

An additional consideration is that, a distinct and persistent period of relative high water occurs in the lower Willamette from late May through June when spring freshet-driven high flows in the Columbia increase the hydraulic head at the confluence of the two rivers and cause the flow of the Willamette to be detained (LWG 2004). When this occurs, water volume in the Willamette is increased irrespective of its flow. To account for this detention, channel cross section area was estimated as a function of river stage (STAGE), rather than flow, with STAGE estimated from USGS observations at RM 12.8 between 1987 and 2005. Thus $\text{XSA} = 788.95 * \text{STAGE} + 35043$ ($R^2 = 0.84$) in the upper harbor and $\text{XSA} = 788.95 * \text{STAGE} + 45000$ in the lower harbor.

The velocity apportionment factor (UAF) derives from the assumption, based on data collected in the lower harbor, that velocity in side segments (those in contact with the shore and in shallower water) will be approximately 75% of that in the center (main channel) segment (Krcma et al. 2002). The Excel Goal Seek™ tool was used to estimate a value for UAF in the center segment so that the relationship $U = Q/\text{XSA}$ was maintained and the sum of the flows across each segment equals that for the entire river. Resulting UAF values were 0.89, 1.186, 1.066, and 1.422 for upper river side, upper river center, lower river side, and lower river center segments, respectively. The cross-section apportionment factor (XAF) is then the width of a segment divided by the sum of it and its adjacent segments (WID_T). Neither UAF or XAF were applied to the Shipyard Lagoon (segment 37).

2.4.2. LATERAL FLUX ESTIMATION

The movement of a chemical laterally between adjacent segments is estimated as a function of the relative difference in chemical concentration between the side segments and the average concentration across all three adjacent segments (Figure 5). This flow is driven by that in the center segment.

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$$FQX = (QA_{\text{center}} \cdot CF_{MF} \cdot CF_{LM}) \cdot (CWT_{\text{side}} - CWT_{\text{avg}}) \cdot CF_{NK} \quad (5)$$

where: FQX = Flux between adjacent segments (kg d^{-1}); QA_{center} = Apportioned mean of daily flow from the center segment ($\text{ft}^3 \text{s}^{-1}$), CF_{MF} = Conversion factor ($2446.5755 \text{ m}^3 \text{ft}^{-3} \cdot \text{s d}^{-1}$), CF_{NK} = Conversion factor ($1 \times 10^{-12} \text{ kg ng}^{-1}$), CWT_{side} = Total chemical water concentration in side segment (ng L^{-1}), and CWT_{avg} = Average total chemical water concentration in three adjacent segments (ng L^{-1}).

2.4.3. TIDALLY-DRIVEN FLUX ESTIMATION

The tidal range at the Pacific Ocean is approximately 1.5 m and there are two high tides and two low tides daily. The tidal “wave” coming up the river can result in flow reversals in the Willamette River near its mouth and within Multnomah Channel under certain river stage, river flow, and tidal conditions (Caldwell and Doyle 1995; LWG 2004). During summer low-flow periods, tidal effects can cause flow reversals in the Willamette River below RM 15. Such reversals are most likely during times of extreme low discharge combined with a large variation in tide levels, which can occur in late summer to early fall. As river stage rises, this tidal effect is gradually dampened and disappears at river levels around 10 feet Columbia River Datum. These flow reversals could serve to transport (via tidal back-flow) sediment-bound chemicals from a chemical source downstream of the domain into segments 34-36. A special case, which applies only to , occurs when these segments are loaded by . The tidally-driven movement of a chemical between segments (Figure 5) is assumed to be a function of the relative difference in chemical concentration between upstream and downstream segments.

$$FQT = (\Delta T \cdot CF_{MF} \cdot CF_{LM}) \cdot (CWT_{\text{dn}} - CWT_{\text{up}}) \cdot CF_{NK} \quad (6)$$

$$\text{if}(QT + Q < 0) \text{ then } \Delta T = QT + QA \text{ else } \Delta T = 0 \quad (7)$$

$$QT = 3500 \cdot \cos(4 \cdot \pi \cdot t) \quad (8)$$

where: FQT = Flux due to tidally-driven flow (kg d^{-1}), QT = Tidal flow ($\text{ft}^3 \text{s}^{-1}$), CWT_{dn} = Total chemical water concentration in the downstream segment (ng L^{-1}), CWT_{up} = Total chemical water concentration in the upstream segment (ng L^{-1}), ΔT = Differential between downstream flow and cyclical tidal flow ($\text{ft}^3 \text{s}^{-1}$), and t = time (d). Equation 7 is structured so that tidal reversals, of up to $\approx -3,500 \text{ ft}^3 \text{s}^{-1}$, occur only between mid-June to mid-October, during summer low flow.

2.4.4. EXTERNAL LOAD ESTIMATION

Although various external loads (e.g., from overland flows, outfalls, groundwater upwelling,

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bank erosion, etc.) are possible, this study focuses on four: those from stormwater (SWL), upstream (USL) and downstream (DSL) sources, and direct deposition from the atmosphere to water (FAW). Any direct loading of the active sediment layer by, for example, a legacy contaminant source buried in a deeper sediment layer, is not considered. A USL is applied only to Segments 1 - 3 as a function of mainstem flow and the surface water concentration at or near RM 12.0, the southern boundary of the model domain. A DSL is applied only to Segments 34 - 36 as a function of tidally-driven backflows and the surface water concentration at or below RM 1.8, the northern boundary of the model domain.

Contributions from wet and dry atmospheric deposition direct to water (FAW), and to land within the watershed of the ISA, were calculated as described in Mackay et al. (1994),

$$D_{\text{dry-p}} = (UD \cdot A \cdot \text{FSA} \cdot \text{CTA}) / 1000 \quad (10)$$

$$D_{\text{dry-g}} = (VE \cdot A \cdot (1 - \text{FSA}) \cdot \text{CTA}) / (1000 \cdot \text{KAW}) \quad (11)$$

$$D_{\text{wet-p}} = (UR \cdot A \cdot \text{FSA} \cdot \text{CTA} \cdot W_p) / 1000 \quad (12)$$

$$D_{\text{wet-g}} = (UR \cdot A \cdot (1 - \text{FSA}) \cdot \text{CTA} \cdot W_g) / 1000 \quad (13)$$

$$L_{\text{land}} = (\delta \cdot \text{CSW}_T \cdot \text{CF}_{\text{NK}}) \quad (14)$$

where: $D_{\text{dry-p}}$ = Dry deposition, particles (kg d^{-1}), UD = Dry deposition velocity (m d^{-1}), A = Water or watershed (land) surface area (m^2), FSA = Fraction of chemical absorbed to aerosols (unitless), CTA = Total average contaminant concentration in air (g m^{-3}), $D_{\text{dry-p}}$ = Dry deposition, gaseous (kg d^{-1}), VE = Overall water-side mass transfer coefficient (m d^{-1}), KAW = Air-water partition coefficient (unitless), $D_{\text{wet-p}}$ = Wet deposition, particles (kg d^{-1}), UR = Rainfall rate (m d^{-1}), W_p = Particle scavenging ratio (unitless), $D_{\text{wet-g}}$ = Wet deposition, gaseous (kg d^{-1}), W_g = Gaseous scavenging ratio (unitless), L_{land} = Load from land-based sources (kg d^{-1}), δ = Mean daily stormwater flow as a function of rainfall ($1.581 \times 10^{10} \times UR^{0.9676}$, L d^{-1}), and CSW_T = Total chemical concentration in stormwater discharging to a given segment (ng L^{-1}). The Harbor watershed area (A) is $5.85 \times 10^7 \text{ m}^2$ (Liebe and Savage 2006). Congener ambient air concentrations were measured at a semi-rural location in the central Willamette Valley and may thus under-represent congener concentrations in Portland urban air (Offenberg and Baker 1997).

Atmospheric deposition to land (FAL) was the sum of wet and dry particulate deposition ($D_{\text{wet-p}}$, $D_{\text{dry-p}}$) plus wet gaseous deposition ($D_{\text{wet-g}}$). Wet deposition to land was transferred directly to the river, via stormwater, when a rainfall event exceeded a threshold of 0.00254 m (0.1 inch) over a 24 hour period; events less than 0.00254 m were considered to be non-runoff

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producing due to rainfall interception and depression storage (Liebe and Savage 2006). Dry deposition to land was also transferred directly to the river, via stormwater, when a rainfall event exceeded 0.00254 m. When a rain event did not occur or was < 0.00254 m, the dry particulate deposition load was accumulated, then discharged as a pulse at the next qualifying event (Rossi et al. 2004). Dry gaseous deposition (D_{dry-g}) was estimated for water, but not land, surfaces. Atmospheric deposition direct to water (FAW) was estimated as the sum of all four types of deposition but was not limited by threshold rainfall events.

The contaminant load conveyed by stormwater (SWL) from land to a given segment of the river is a function of the contaminant load from atmospheric deposition to land (wet and dry particulate plus wet gaseous), any contaminant load from land-based sources, and the fraction of total stormwater flow discharging to that segment (c.f., Figure 3). The Harbor watershed covers an area of $5.85 \times 10^6 \text{ m}^2$ and is divided into 19 sub-watersheds to align with the segments in the river (Liebe and Savage 2006). The air deposited load available for conveyance by stormwater into a given segment is a function of the impervious surface area in the sub-watershed draining into that segment (c.f., Figure 3).

$$SWL = (L_{land} + (D_{wet-p} + D_{wet-g} + D_{dry-p}) \cdot IP_{frac}) \cdot SW_{frac} \quad (15)$$

where: SWL = Total load conveyed to a given river segment via stormwater (kg d^{-1}), IP_{frac} = Fraction of impervious land in the sub-watershed (unitless), and SW_{frac} = Fraction of total stormwater flow discharging from that sub-watershed to a given river segment (unitless).

Gustafsson and Gschwend (1997) advocate a particle classification scheme that separates runoff-related contaminants into four fractions (dissolved, colloidal, gravitoidal, and sediment) based on the expected behavior of contaminants within each fraction. These contaminant fractions cannot be cleanly divided on the basis of a single set of arbitrary cutoffs with respect to particle size (Farley and Morel 1986, Grant et al. 2001, Logan 1995). Contaminants dynamically transfer between fractions by sedimentation, erosion, coagulation, fragmentation, adsorption, and desorption. While recognizing these nuances, this model treats SWL as a total contaminant load to the water column and allows contaminant partitioning between dissolved and particle-bound phases to occur only within the water column, as opposed to during stormwater conveyance to the river.

2.4.5. SOLIDS SETTLING RATE

The solids settling rate (VSS) is a particularly sensitive variable in this model. The Willamette from RM 9.2 to approximately RM 7 is a net depositional area, hence the requirement for periodic dredging. From RM 7 to RM 3.5 it is predominantly a system in

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equilibrium, with some localized areas of deposition and erosion. Deposition rates for the navigation channel (i.e., center segments) from RM 7 to 9 have been estimated in the range of 0.0004 to 0.0008 m d⁻¹ (0.5 to 1.0 ft yr⁻¹) (LWG 2004). Most of this deposition occurs in bathymetric lows commonly associated with dredging areas, and along the inside bends of the river. Erosion is most consistent outside of the Harbor, but occurs in localized areas such as along the outside bends of the river, due to short-term hydrologic events (LWG 2004). In recognition of the deposition potential noted between RM 7 and 9, the value of VSS was set at 0.001 m d⁻¹ in center Segments 8, 11, and 14 but at 0.0 m d⁻¹ in all other center segments. Settling rates in all side segments were assumed to equal the maximum rate measured in a backwater area of the harbor (T4, Berth 401): 129 g cm⁻² yr⁻¹ or VSS = 0.002 m d⁻¹. In comparison, deposition rates in the lower Fraser River have been estimated at 0.9 to 1.8 cm yr⁻¹ (2.5×10^{-5} m d⁻¹ to 5×10^{-5} m d⁻¹) (Gobas et al. 1998). Burial to deeper sediment was assumed to be unlikely in this active river system, thus VB was set to 0.0 m d⁻¹ in all segments.

2.5. FOOD WEB MODEL

Algorithms and variables for the food web model are described in Arnot and Gobas (2004) and are summarized in Table 3. The last five terms in Table 4 relate to calculation of the bioavailable solute fraction as described by Arnot and Gobas (2004) and Gobas and Arnot (2005). The model food web includes ten aquatic species that surveys and sampling activities have found in the Harbor, particularly its near-shore areas (LWG 2004, USEPA 2006). These include phytoplankton, zooplankton, filter-feeding benthic invertebrates (clams, *Corbicula*), benthic consumer invertebrates (oligochaete worms), epibenthic consumer invertebrates (crayfish), forage fish (sculpin, *Cottus* sp.), benthivorous fish (largescale sucker, *Catostomus macrocheilus*), omnivorous fish (common carp, *Cyprinus carpio*), carnivorous fish (smallmouth bass, *Micropterus dolomieu*), and piscivorous fish (northern pikeminnow, *Ptychocheilus oregonensis*). The feeding relationships between these species, based on literature surveys and the results of stomach content analyses on fish collected within the Harbor, are summarized in Table 4. Uncertainty in the true value of certain variables is represented, when possible, with uniform distributions (Tables 3 and 4); dietary fractions are normalized to one before use in any calculations.

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3. RESULTS AND DISCUSSION

3.1. GENERAL

When interpreting the model estimates, potential impacts to sediment were evaluated using the Oregon Department of Environmental Quality screening level value (SLV) for sediment (ODEQ 2006, Table A-1b). Potential impacts to fish consumers were assessed (for carcinogenic effects) with the Oregon Department of Environmental Quality acceptable tissue level (ATL) for the general human population (ODEQ 2006, Table A-3b) and (for non-carcinogenic effects) with the U.S. EPA fish consumption advisory value (FCAV) for unrestricted fish consumption by the general human population (USEPA 2000).

Portland Harbor Round 2 sediment and surface water data (USEPA 2006) were used to estimate, respectively, the mean total contaminant concentration in sediment (CST) in each segment and the average total contaminant concentration in surface water upstream of the model domain (CWT_{up}) for each individual contaminant (Table 5). No data were available with which to estimate total water concentrations (CWT_{out}) downstream of the domain. For Scenario 6, the initial mass of contaminant in the sediment compartment of each segment was adjusted until the estimated sediment concentration (CST) closely approximated the observed mean value. Alignment between modeled and observed CST values was assessed by the sum of the square of their differences (Σ SQDiff); values closer to zero indicate greater alignment. For all contaminants, the model could not replicate the presently observed spatial distribution and magnitude of sediment concentrations on a segment-by-segment basis by applying only continuous or episodic upstream, atmospheric deposition, or stormwater loads. The highly heterogeneous pattern of contamination observed in sediment could only be replicated as described above, which suggests that it is most likely tied to specific past (legacy) or present (continual or episodic) releases at discrete points within the Harbor.

The smallmouth bass (SMB), an upper trophic level carnivorous species that is also popular with recreational and subsistence anglers, was selected as a representative species for this study. Portland Harbor Round 1 tissue data (USEPA 2006) were used to estimate the mean total contaminant concentration in this species on a Harbor-wide basis. Levels of specific PCB congeners in smallmouth bass have also been reported elsewhere (Sethajintanin et al. 2004). As was the case with sediment, the model could not replicate the presently observed spatial distribution and magnitude of fish tissue concentrations on a segment-by-segment basis simply by applying various external loads. Interpretation of tissue results was hampered by too few fish samples relative to the size of the Harbor and lack of samples in specific segments (a

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consequence of segments having been delineated following collection of Round 2 samples), which necessitated representing tissue levels in some segments based on width-of-river composite samples.

3.2. PCB-118

Observed and estimated concentrations under the various scenarios are summarized in Table 6A. With only an upstream load (Scenario 1), estimated Harbor-wide mean fish tissue concentrations (\pm one standard deviation) are below the FCAV, but not the ATL in the main river, and well below the ATL in Swan Island lagoon, in both the main river and Swan Island Lagoon; sediment concentrations are below the SLV in all segments. Atmospheric deposition direct to water and conveyed from land via stormwater (Scenario 2) has no significant impact on sediment levels and increases fish tissue levels in the main river by only a negligible amount ($0.064 \pm 0.044 \mu\text{g kg}^{-1}$). Runoff of atmospheric deposition could have a significant impact on fish tissue levels in the Lagoon, where estimated levels ($6.494.8 \mu\text{g kg}^{-1}$) attributable to stormwater are well above both the FCAV and ATL (Scenarios 2 & 3). The Lagoon is a backwater embayment of the main channel within which water movement, and thus any contaminant flushing or dilution, is much lower than in the faster-flowing main river. It also receives the second highest fraction (10.1%) of total stormwater discharges to the Harbor. This combination of low water movement and high loading potentially contribute to elevated tissue levels. When observed sediment concentrations are in every segment (Scenario 6), and all non-negotiable loads are included, fish tissue concentrations exceed both the FCAV and ATL in all segments. In the river (excluding the Lagoon), the relative contribution of upstream, stormwater, and current sediment loads to fish tissue concentrations is estimated to be 45.89.4%, 0.21%, and 84.090.5%, respectively. In the Lagoon, the relative contribution from these loads to tissue levels is estimated to be 4.40.6%, 83.831.4%, and 44.668.0%, respectively. Observed and estimated sediment and tissue concentrations can be compared at Scenario 6. On a Harbor-wide mean basis, there is close agreement in sediment concentrations and an approximately 4-fold difference in tissue levels (Table 6A). The maximum total concentration of PCB-118 in stormwater that will maintain total sediment concentrations below the SLV in every segment (other than the Lagoon) is 125 ng L^{-1} (Scenario 4). When all non-negotiable loads are included, there is no concentration in stormwater $> 0 \text{ ng L}^{-1}$ that will maintain fish tissue concentrations below either the FCAV or ATL in every segment, including the Lagoon (Scenario 5), because these concentrations are already exceeded with the input of upstream and atmospheric loads. When the sediment concentration in every segment

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is set to the SLV (Scenario 7), and all non-negotiable loads are included, fish tissue concentrations are between the FCAV and ATL in the main river; both are exceeded in Swan Island Lagoon.

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4. REFERENCES

- Altman B, Henson CM, and Waite IR. 1997. Summary of Information on Aquatic Biota and Their Habitats in the Willamette Basin, Oregon, through 1995. Water-Resources Investigations Report 97-4023, U.S. Geological Survey, Portland, OR.
- Arnot J and Gobas FAPC. 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environmental Toxicology and Chemistry* 23(10): 2343-2355.
- Breivik K, Bjerkgeng B, Wania F, Helland A, and Magnusson J. 2004. Modeling the fate of polychlorinated biphenyls in the Inner Oslofjord, Norway. *Environmental Toxicology and Chemistry* 23(10): 2386-2395.
- Burkhard LP. 2000. Factors influencing the design of bioaccumulation factor and biota-sediment accumulation factor field studies. *Environmental Toxicology and Chemistry* 22(2): 351-360.
- Caldwell JM and Doyle MC. 1995. Sediment oxygen demand in the Lower Willamette River, Oregon. Water-Resources Investigations Report 95-4196. U.S. Geological Survey, Portland, Oregon.
- Cleverly D, Ferrario J, Byrne C, Riggs K, Joseph D, and Hartford P. 2007. A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States. *Environmental Science & Technology* [online 1/17/2007].
- Liebe M and Savage G. 2006. Various TSS analyses and comparisons - Portland Harbor and Willamette mainstem. Systems Analysis Group, Bureau of Environmental Services, City of Portland, Oregon (memorandum to dated 11 October 2006).
- Cotham WE and Bidleman TF. 1991. Estimating the atmospheric deposition of organochlorine contaminants to the Arctic. *Chemosphere* 22: 165-188.
- Davis JA. 2003. The long term fate of PCBs in San Francisco Bay. RMP Technical Report: SFEI Contribution 47. San Francisco Estuary Institute, Oakland, CA.
- Davis JA. 2004. The long term fate of PCBs in San Francisco Bay. *Environmental Toxicology and Chemistry* 23(10): 2396-2409.
- Diamond ML, Mackay D, Poulton DJ and Stride FA. 1996. Assessing chemical behavior and developing remedial actions using a mass balance model of chemical fate in the Bay of Quinte. *Water Research* 30(2): 405-421.
- Duinker JC and Bouchertall F. 1989. On the distribution of atmospheric polychlorinated biphenyl congeners between vapor phase, aerosols, and rain. *Environmental Science and*

WORKING DRAFT

Technology 23(1): 57-62.

Durrell GS and Lizotte Jr RD. 1998. PCB levels at 26 New York City and New Jersey WPCPs that discharge to the New York/New Jersey harbor estuary. *Environmental Science & Technology* 32(8): 1022-1031.

Farley JK and Morel FMM. 1986. Role of coagulation in the kinetics of sedimentation. *Environmental Science & Technology* 20(2): 187-195.

Frame, GM, Wagner RE, Carnahan JC, Brown Jr JF, May RJ, Smullen LA, and Bedard DL 1996. Comprehensive, quantitative, congener-specific analyses of eight Aroclors and complete PCB congener assignments on DB-1 capillary GC columns. *Chemosphere* 33(4): 603-623.

Gobas FAPC and Arnot J. 2005. San Francisco Bay PCB food web bioaccumulation model: Final technical report. CEP Task 4.27. Clean Estuary Partnership, San Francisco, CA (www.cleanestuary.com/publications/index.cfm?fuseaction=details&docid=61).

Gobas FAPC, Pasternak JP, Lien K and Duncan RK. 1998. Development and field validation of a multimedia exposure assessment model for waste load allocation in aquatic ecosystems: Application to 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran in the Fraser River watershed. *Environmental Science and Technology* 32: 2442-2449.

Gobas FAPC, Z'Graggen MN and Zhang X. 1995. Time response of the Lake Ontario ecosystem to virtual elimination of PCBs. *Environmental Science and Technology* 29: 2038-2046.

Grant SB, Kim JH and Poor C. 2001. Kinetic theories for the coagulation and sedimentation of particles. *Journal of Colloidal and Interface Science* 238: 238-259.

Greenfield BK and Davis JA. 2004. A simple mass balance model for PAH fate in the San Francisco Estuary. RMP Technical Report, SFEI Contribution 115. San Francisco Estuary Institute, Oakland, CA.

Gustafsson O. and Gschwend, PM. 1997. Aquatic colloids: Concepts, definitions, and current challenges. *Limnology and Oceanography* 42: 519-528.

Hawker DW and Connell DW. 1988. Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environmental Science and Technology* 22: 382-387.

Henny CJ, Kaiser JL, Grove RA, Bentley VR and Elliott JE. 2003. Biomagnification factors (fish to osprey eggs from Willamette River, Oregon, U.S.A.) for PCDDs, PCDFs, PCBs, and OC pesticides. *Environmental Monitoring and Assessment* 84: 275-315.

Hornbuckle KC, Jeremiason JD, Sweet CW and Eisenreich SJ. 1994. Seasonal variation in air-

WORKING DRAFT

- water exchange of polychlorinated biphenyls in Lake Superior. *Environmental Science and Technology* 28: 1491-1501.
- Jantunen LM and Bidleman TF. 2006. Henry's law constants for hexachlorobenzene, p,p'-DDT and components of technical chlordane and estimates of gas exchange for Lake Ontario. *Chemosphere* 62(10): 1689-1696.
- Krcma K, Hermans M, and Hardin D. An inland tombolo affects maintenance dredging at Berth 501, Port of Portland. Parsons Brinkerhoff Technical Paper. Parsons Brinkerhoff Quade & Douglas, Portland, OR (http://www.pbworld.com/library/technical_papers/pdf/14_AnInlandTombolo.pdf).
- Laenen A and Risley JC. 1997. Precipitation-Runoff and Streamflow-Routing Models for the Willamette River Basin, Oregon. Water-Resources Investigations Report 95-4284. U.S. Geological Survey, Portland, Oregon.
- Logan BE. 1995. Comment on investigation of a sequential filtration technique for particle fractionation. *Environmental Science and Technology*, 29(N8):2166-2167.
- Loganathan BG, Irvine KN, Kannan K, Pragasheeswaran V and Sajwan KS. 1997. Distribution of selected PCB congeners in the Babcock Street Sewer District: A multimedia approach to identify PCB sources in combined sewer overflows (CSOs) discharging to the Buffalo River, New York. *Environmental Contamination and Toxicology* 33(2): 130-140.
- LWG (Lower Willamette Group). 2004. Portland Harbor RI/FS Programmatic Work Plan. Lower Willamette Group, Portland, OR (<http://yosemite.epa.gov/R10/CLEANUP.NSF/ph/Technical+Documents>).
- Mackay D and Hickie B. 2000. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. *Chemosphere* 41: 681-692.
- Mackay D, Sang S, Vlahos P, Diamond M, Gobas F and Dolan D. 1994. A rate constant model of chemical dynamics in a lake ecosystem: PCBs in Lake Ontario. *Journal of Great Lakes Research* 20(4): 625-642.
- Mackay D, Shiu WY and Ma KC. 1992a. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate of Organic Chemicals, Volume I - Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs. Lewis Publishers, Boca Raton, Florida.
- Mackay D, Shiu WY and Ma KC. 1992b. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate of Organic Chemicals, Volume II - Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Lewis Publishers, Boca Raton, Florida.
- Mackay D. 2001. Multimedia Environmental Models: The Fugacity Approach, Second Edition.

WORKING DRAFT

2001. Lewis Publishers, Boca Raton, FL.
- Mandalakis M and Stephanou EG. 2004. Wet deposition of polychlorinated biphenyls in the eastern Mediterranean. *Environmental Science and Technology* 38: 3011-3018.
- MOE (Ministry of the Environment). 2001. Phase II Moira River Study, Impacts of the Former Deloro Mine Site on the Moira River System. Chapter 4: Predictive Water and Sediment Quality Model. Ontario Ministry of the Environment, Canada (<http://www.ene.gov.on.ca/envision/deloro/moira.htm>).
- ODEQ (Oregon Department of Environmental Quality). 2006. Guidelines for Assessing Bioaccumulative Chemicals of Concern in Sediment (Final). Environmental Cleanup Program, Portland, Oregon (<http://www.deq.state.or.us/wmc/pubs/docs/cu/GuidelinesAssessingBioaccumulativeChemicalsInSediment.pdf>).
- Offenberg JH and Baker JE. 1997. Polychlorinated biphenyls in Chicago precipitation: Enhanced wet deposition to near-shore Lake Michigan. *Environmental Science and Technology* 31: 1534-1538.
- Paasivirta J, Sinkkonen S, Mikkelsen P, Rantio T, and Wania F. 1999. Estimation of vapor pressures, solubilities, and Henry's Law constants for selected persistent organic pollutants as functions of temperature. *Chemosphere* 39(5): 811-832.
- Patterson DG, et al. 1994. Levels of non-ortho-substituted (coplanar), mono- and di-ortho-substituted polychlorinated biphenyls, dibenzo-*p*-dioxins, and dibenzofurans in human serum and adipose tissue. *Environmental Health Perspectives Supplements* 102 Suppl. 1: 195-204.
- Rossi L, de Alencastro L, Kupper T, and Tarradellas J. 2004. Urban stormwater contamination by polychlorinated biphenyls (PCBs) and its importance for urban water systems in Switzerland. *Science of the Total Environment* 322: 179-189.
- Sethajintanin D and Anderson KA. 2006. Temporal bioavailability of organochlorine pesticides and PCBs. *Environmental Science and Technology* 40(12): 3689-3695.
- Sethajintanin D, Johnson ER, Loper BR and Anderson KA. 2004. Bioaccumulation profiles of chemical contaminants in fish from the Lower Willamette River, Portland Harbor, Oregon. *Archives of Environmental Contamination and Toxicology* 46: 114-123.
- Ten Hulscher TEM, Van Der Velde LA, and Bruggerman WA. 1992. Temperature dependence of HLCs for selected chlorobenzenes, PCBs, and PAHs. *Environmental Toxicology and Chemistry* 11: 1595-1603.
- Ulrich MA and Wentz DA. 1999. Environmental Setting of the Willamette Basin, Oregon. Water Resources Investigations Report 97-4082-A, U.S. Geological Survey, Portland, OR.

WORKING DRAFT

- USEPA (U.S. Environmental Protection Agency). 2006. Portland Harbor Cleanup Site, Technical Document Repository. Region 10, U.S. Environmental Protection Agency, Seattle, WA (<http://yosemite.epa.gov/R10/CLEANUP.NSF/ph/Technical+Documents>).
- USEPA (U.S. Environmental Protection Agency). 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 2. EPA 823-B-00-008. Office of Water, U.S. Environmental Protection Agency, Washington, DC.
- Van den Berg, M et al. 2005. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences* 93(2): 223-241.
- Windward. 2005. Food Web Modeling Report: Evaluating TrophicTrace and the Arnot and Gobas Models for Application to the Portland Harbor Superfund Site (Draft). Windward Environmental LLC, Seattle, WA (<http://yosemite.epa.gov/R10/CLEANUP.NSF/ph/Technical+Documents>).
- Woodward DG, Gannett MW, and Vaccaro J.J. 1998. Hydrogeologic Framework of the Willamette Lowland Aquifer System, Oregon and Washington. USGS Professional Paper 1424-B, U.S. Geological Survey, Portland, OR.

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TABLE 1. Key physicochemical and toxicological properties of selected congeners.

VARIABLE	SYMBOL	CONGENER [CASRN]			
		PCB-077 [32598-13-3]	PCB-118 [31508-00-6]	PCB-126 [57465-28-8]	PCB-169 [32774-16-6]
TEF _{WHO05} ^(a)	---	0.0001	0.00003	0.1	0.03
Water-side evaporation mass transfer coefficient (m d ⁻¹) ^(d)	VEW	0.656 ^(h)	0.649	0.649 ^(e)	0.632 ⁽ⁱ⁾
Air-side evaporation mass transfer coefficient (m d ⁻¹) ^(d)	VEA	433 ^(h)	423	423 ^(e)	413 ⁽ⁱ⁾
Water-to-sediment mass transfer coefficient (m d ⁻¹) ^(d)	VE	0.0012 ^(h)	0.0024	0.0024 ^(e)	0.0048 ⁽ⁱ⁾
Henry's Law constant (Pa m ³ mol ⁻¹) ⁽ⁱ⁾	H	exp(12.86 - 3213/TW)	exp(13.44 - 3535/TW)	exp(14.03 - 3830/TW)	exp(14.76 - 3910/TW)
Octanol-water partition coefficient (unitless) ^(b)	KOW	6.36	6.74	6.89	7.42
Half-life, water (d)	---	420 ^(f)	2000 ^(c)	2000 ^(e)	2300 ^(g)
Half-life, sediment (d)	---	2300 ^(f)	4200 ^(c)	4200 ^(e)	7100 ^(g)
Particle scavenging ratio (unitless) ^(l)	W _P	360000 ± 140000 ^(m)	330000 ± 150000	330000 ± 150000 ^(e)	240000 ± 110000 ⁽ⁿ⁾
Vapor scavenging ratio (unitless) ^(l)	W _G	12000 ± 4000 ^(m)	25000 ± 4000 ^(o)	25000 ± 4000 ^(o)	5300 ± 3300 ⁽ⁿ⁾

^(a) WHO toxic equivalent factor (Van den Berg et al. 2005).

^(b) Hawker and Connell (1988).

^(c) Breivik et al. (2004).

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- (d) Values from Davis (2003), unless indicated otherwise.
- (e) Value for PCB-118.
- (f) Value for PCB-052 (Breivik et al. 2004).
- (g) Value for PCB-153 (Breivik et al. 2004).
- (h) Value for PCB-066.
- (i) Value for PCB-153.
- (j) Henry's Law temperature dependence (Paasivirta et al. 1999); TW = water temperature $^{\circ}K$.
- (k) Willamette Basin (Cleverly et al. 2007).
- (l) Arithmetic mean \pm one standard deviation (Mandalakis and Stephanou 2004).
- (m) Value for PCB-074.
- (n) Value for PCB-174.
- (o) Value for PCB-132.

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TABLE 2. Summary of transport and fate model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Water surface area of a segment (m ²)	SAW	= LEN × WID	---
Segment length (m)	LEN	Figure 3	NOAA Chart 18526 and U.S. EPA, <i>personal communication</i> .
Segment width (m)	WID	Side segments: 10 Center segments (upper): 380 Center segments (lower): 480	NOAA Chart 18526 and estimate of 15 m depth contour.
Sediment surface area of a segment (m ²)	SAS	---	Assumed equal to water surface area (SAW)
Sediment volume of a segment (m ³)	VS	= SAS × AD	---
Active sediment depth in a segment (m)	AD	0.28	Maximum depth to which sediment samples were collected.
Water temperature (C°)	TW	= 7.812 * cos(0.01717 * t - 3.627) + 13.34	Function estimated from USGS observations at RM 12.8 from 1974 - 2004.
Mean of daily mean flow (ft ³ s ⁻¹)	Q	Varies	Estimated from USGS observations at RM 12.8 from 1972 - 2004.
Concentration of particles in water (kg L ⁻¹)	CPW	Segment 1-36: = 6.83 × 10 ⁻⁶ * exp(1.81 × 10 ⁻⁵ * Q) Segment 37: 0.078	Function for segments 1-36 estimated from USGS observations at RM 12.8 from 1978 - 2004. Value for segment 37 from Windward (2005).
Concentration of solids in sediment (kg L ⁻¹)	CSS	0.5	Default assumption, based on Davis (2004).
Density of particles (suspended solids) in water (kg L ⁻¹)	DPW	1.1	Default assumption, based on Davis (2004).
Density of solids in sediment (kg L ⁻¹)	DSS	2.0	Default assumption, based on Gobas et al. (1995).
Suspended solids settling rate (m d ⁻¹)	VSS	Side segments: 0.002 Center segments: 0.0	See text
Organic carbon content of suspended solids (unitless)	OCPW	Segments 1-36: 0.0184 Segment 37: 0.0202	Harbor-specific empirical data, cited in Windward (2005).
Organic carbon content of bottom sediment (unitless)	OCSS	---	Assumed to be the same as OCPW.
Sediment solids burial rate (m d ⁻¹)	VB	0.0	Default assumption.

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TABLE 2. Summary of transport and fate model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Dry deposition velocity (m d^{-1})	UD	240	Mackay et al. (1994)
Fraction of contaminant on aerosols (unitless)	FSA	0.30	Duinker and Bouchertall (1989)
Mean daily rainfall rate (m d^{-1})	UR	Figure 6	NOAA precipitation data for the City of Portland, Oregon
Fraction of total stormwater flow entering segment (unitless)	SW_{frac}	Figure 3	Liebe and Savage (2006)
Impervious fraction of total watershed area (unitless)	IP_{frac}	Figure 3	Estimated from data provided by Liebe and Savage (2006)

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TABLE 3. Summary of Harbor-specific food web model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Uptake constant A (unitless)	UA	0.0006	Arnot and Gobas 2004; Eq. 10
Uptake constant B (unitless)	UB	5.50	Arnot and Gobas 2004; Eq. 10
Dietary transfer efficiency constant A (unitless)	EDA	3×10^{-7}	Arnot and Gobas 2004; Eq. 13
Dietary transfer efficiency constant B (unitless)	EDB	2.00	Arnot and Gobas 2004; Eq. 13
Non-lipid organic matter (NLOM) – octanol proportionality constant (unitless)	BETA	0.08	Arnot and Gobas 2004; Eq. 3
Non-lipid organic carbon (NLOC) – octanol proportionality constant (unitless)	GAMMA	0.35	Arnot and Gobas 2004
Organism weight (kg) ^(a)	WB	PHY: n/a	Windward 2005
		ZOO: U[2.3×10^{-6} , 3.3×10^{-6}] ^(b)	
		BFI: U[0.005, 0.006]	
		BCI: U[1.4×10^{-6} , 6.0×10^{-6}]	
		ECI: U[0.034, 0.048]	
		SCL: U[0.014, 0.03]	
		LSS: U[0.748, 0.864]	
		CAR: U[2.15, 2.79]	
		SMB: U[0.264, 1.23]	
Filter feeder scavenging efficiency (unitless)	SCV	NPM: U[0.440, 0.719]	Assumed
		BFI: 1	
Growth rate constant (d ⁻¹)	KG	Zero for all other species	Windward 2005
		PHY: U[0.03, 0.13]	
Metabolic rate constant (d ⁻¹)	KM	Calculated for all other species	Assumed
		Zero in all species	

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TABLE 3. Summary of Harbor-specific food web model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Lipid fraction of organism (kg kg ⁻¹)	VLB	PHY: ([0.935, 0.993]	Windward 2005
		ZOO: U[0.009, 0.011]	
		BFI: U[0.008, 0.017]	
		BCI: U[0.008, 0.012]	
		ECI: U[0.002, 0.013]	
		SCL: U[0.006, 0.022]	
		LSS: U[0.054, 0.087]	
		CAR: U[0.056, 0.13]	
		SMB: U[0.015, 0.072]	
		NPM: U[0.023, 0.081]	
Water content fraction of organism (kg kg ⁻¹)	VLW	PHY: ([0.001, 0.002]	Windward 2005
		ZOO: 0.9	
		BFI: U[0.872, 0.890]	
		BCI: 0.8	
		ECI: U[0.693, 0.771]	
		SCL: U[0.728, 0.787]	
		LSS: U[0.697, 0.734]	
		CAR: U[0.665, 0.720]	
		SMB: U[0.680, 0.785]	
Dietary absorption efficiency of lipid (%)	eL	PHY: n/a	Windward 2005
		ZOO: 0.72	
		BFI, BCI, ECI: 0.75	
		SCL, LSS, CAR, SMB, NPM: 0.92	

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TABLE 3. Summary of Harbor-specific food web model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Dietary absorption efficiency of NLOM (%)	eN	PHY: n/a ZOO: 0.72 BFI, BCI, ECI: 0.75 SCL, LSS, CAR, SMB, NPM: 0.55	Windward 2005
Dietary absorption efficiency of water (%)	eW	PHY: n/a ZOO, BFI, BCI, ECI, SCL, LSS, CAR, SMB, NPM: 0.25	Windward 2005
Fraction of sediment pore water ventilated (%)	mp	PHY: 0 ZOO: 0 BFI: U[0.01, 0.05] BCI: U[0.01, 0.09] ECI: 0 SCL: U[0.05, 0.07] LSS: U[0.05, 0.1] CAR: U[0.05, 0.1] SMB: 0 NPM: 0	Windward 2005
Dissolved organic carbon proportionality constant (unitless)	aDOC	0.08	Burkhard (2000)
Particulate organic carbon proportionality constant (unitless)	aPOC	0.35	Arnot and Gobas (2004); Eq. 4
Density of organic carbon in sediment (kg L ⁻¹)	DOCS	0.9	Value for Great Lakes cited in Arnot and Gobas (2004) and Windward (2005).
Dissolved organic carbon concentration in water (kg L ⁻¹)	XDOC	Segments 1-33: 1.6×10^{-6} Segment 34: 1.7×10^{-6}	Cited in Windward (2005)

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TABLE 3. Summary of Harbor-specific food web model input variables.

VARIABLE (units)	SYMBOL	BEST ESTIMATE	COMMENTS
Particulate organic carbon concentration in water (kg L ⁻¹)	XPOC	Segments 1-33: 4.0×10^{-7} Segment 34: 4.2×10^{-7}	Cited in Windward (2005)

NOTES

- (a) Organism code: SP - sediment solids (carbon particles); PHY – phytoplankton; ZOO – zooplankton; BIF – benthic filter-feeding invertebrate; BIC – benthic consumer invertebrate; EIC – epibenthic consumer invertebrate; SCL – sculpin; LSS – largescale sucker; CAR – carp; SMB – small mouth bass; NPM – northern pikeminnow.
- (b) U[minimum, maximum] denotes the minimum and maximum values of a uniform random variable.

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TABLE 4. Aquatic species included in the Harbor-specific food web model and their feeding relationships.

PREY ^(a) ⇔ PREDATOR ↓	SSP	PHY	ZOO	BFI	BCI	ECI	SCL	LSS	CAR	SMB	NPM
SSP											
PHY											
ZOO		1.00									
BIF ^(c)	U[0, 1] ^(b)	U[0, 1]									
BIC ^(c)	U[0.9, 1]	U[0, 0.1]									
ECI	U[0, 0.4]	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]						
SCL ^(c)			U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]					
LSS ^(c)	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]					
CAR ^(c)	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]					
SMB			U[0, 1]	U[0, 1]	U[0, 1]	U[0, 1]					
NPM		U[0, 1]		U[0, 1]	U[0, 1]	U[0, 1]					

NOTES

- ^(a) Organism code: SP - sediment solids (carbon particles); PHY – phytoplankton; ZOO – zooplankton; BIF – benthic filter-feeding invertebrate; BIC – benthic consumer invertebrate; EIC – epibenthic consumer invertebrate; SCL – sculpin; LSS – largescale sucker; CAR – carp; SMB – small mouth bass; NPM – northern pikeminnow.
- ^(b) U[minimum, maximum] denotes the minimum and maximum values of a uniform random variable. The row sum for a given species is normalized to one before entering model calculations.
- ^(c) Indicates species that ventilate sediment porewater as indicated by the *mp* variable (Table 3).

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TABLE 5. Summary of observed contaminant concentrations in various media.

VARIABLE	CONGENER [CASRN] CONCENTRATION §			
	PCB-077 [32598-13-3]	PCB-118 [31508-00-6]	PCB-126 [57465-28-8]	PCB-169 [32774-16-6]
Concentration in surface water upstream - CWT _{up} (pg L ⁻¹) ^(a)	0.68 ± 1.00 0.33 ± 0.28	10.72 ± 9.56 4.34 ± 2.63	0.05 ± 0.04 0.01 ± 0.005	ND ^(b)
Concentration in fish tissue (µg kg ⁻¹)	0.41 ± 0.30 ^(c)	15.45 ± 12.31 ^(c) 27.66 ± 16.39 ^(d)	0.066 ± 0.02 ^(c)	0.003 ± 0.001 ^(c)
Concentration in sediment (µg kg ⁻¹)	1.54 ± 9.87 ^(e) 1.65 ± 10.24 ^(f)	16.70 ± 44.54 ^(e) 14.63 ± 57.53 ^(f, g)	0.07 ± 0.24 ^(e) 0.07 ± 0.25 ^(f)	0.01 ± 0.02 ^(e) 0.04 ± 0.1 ^(f)
Concentration in air (fg m ⁻³) ^(h)	52.7 ± 18.9	1437.9 ± 590.7	5.1 ± 1.2	0.5 ± 0.4

§ Values shown are arithmetic mean ± one standard deviation.

^(a) Portland Harbor, Round 2 (Dec 2004) data (USEPA 2006). Upper value concentration on solid fraction; lower value concentration in dissolved fraction.

^(b) No values reported above detection limit.

^(c) Portland Harbor, Round 1 (Apr 2003) data, smallmouth bass only (USEPA 2006).

^(d) Portland Harbor, RM 3 - 15, smallmouth bass only (Sethajintanin et al. 2004).

^(e) Portland Harbor, Round 1 (Apr 2003) data (USEPA 2006).

^(f) Portland Harbor, Round 2 (Aug 2005) data (USEPA 2006).

^(g) PCB 106 & 118 mixture (USEPA 2006).

^(h) National Dioxin Air Monitoring Network (NDAMN) site near Albany, Oregon (Cleverly et al. 2007).

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Table 6A. Summary of observed and estimated PCB-118 concentrations in sediment and fish tissue by scenario.

Scenario	Description	CONCENTRATION ($\mu\text{g kg}^{-1}$)	
		SEDIMENT	FISH TISSUE
1	Upstream load (USL) only. $\text{CWT}_{\text{up}} = 0.01 \text{ ng L}^{-1}$	0.0013 ± 0.0005 0.00044 (Lagoon)	$4.053.97 \pm 0.0.7269$ $0.121.53$ (Lagoon)
2	Atmospheric deposition to water (FAW) and land (FAL) only	$4.1.48 \times 10^{-5} \pm 1.40.9 \times 10^{-5}$ $0.030.003$ (Lagoon)	$0.00.064 \pm 0.00.042$ $91.86.4$ (Lagoon)
3	Upstream load (USL) and atmospheric deposition to water (FAW) and land (FAL)	0.0013 ± 0.0005 $0.00.0033$ (Lagoon)	$4.4.1901 \pm 0.7.0.731$ $93.46.71$ (Lagoon)
4	Upstream load (USL), atmospheric deposition to water (FAW) and land (FAL), and maximum allowable stormwater load (SWL) ^(a) relative to sediment. $\text{CSW}_T \cong 125 \text{ ng L}^{-1}$	$0.04 \pm 0.0.0.034$ $13.41.5$ (Lagoon)	$11115.90.1 \pm 1009.16.1$ 52140.24429 (Lagoon)
5	Upstream load (USL), atmospheric deposition to water (FAW) and land (FAL), and maximum allowable stormwater load (SWL) ^(a) relative to fish tissue. $\text{CSW}_T = 0 \text{ ng L}^{-1}$	n/a	$4.1901 \pm 0.730.71$ $93.46.71$ (Lagoon)
6	Upstream load (USL), atmospheric deposition to water (FAW) and land (FAL), and load from existing sediment contamination (CST) ^(b)	22.2 ± 81.1 8.4 (Lagoon) 16.7 ± 44.5 8.8 (Lagoon)	42.3 ± 141.3 $107.520.9$ (Lagoon) $15.431.2 \pm 12.314.9$ 40.5 ± 20.3 (Lagoon)
7	Upstream load (USL), atmospheric deposition to water (FAW) and land (FAL), and load from sediment at the SLV (CST = SLV)	0.12 ± 0.002 0.12 (Lagoon)	$4.284.17 \pm 0.730.69$ $93.86.86$ (Lagoon)
---	Threshold levels ^(c)	SLV = 0.12	FCAV = 5.9 ^(d) ATL = 2.1

^(a) SWL = FAL (air deposition runoff load from land) + CSW_T (land-based source load).

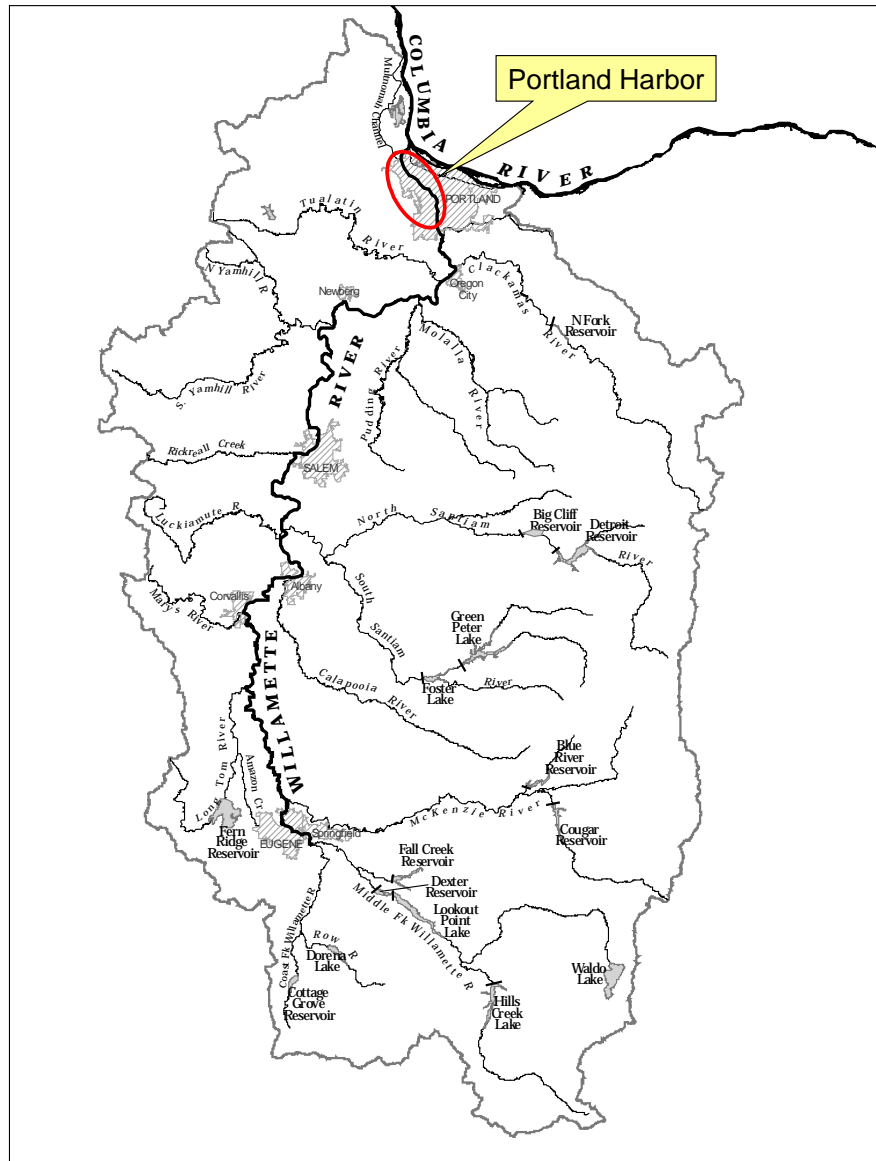
^(b) Observed values shown in italics.

^(c) SLV = Screening level value for sediment; FCAV = Fish consumption advisory value (non-cancer) for general human consumption; ATL = Acceptable tissue level (cancer) for general human consumption.

^(d) Value for total PCBs, non-carcinogenic health effects.

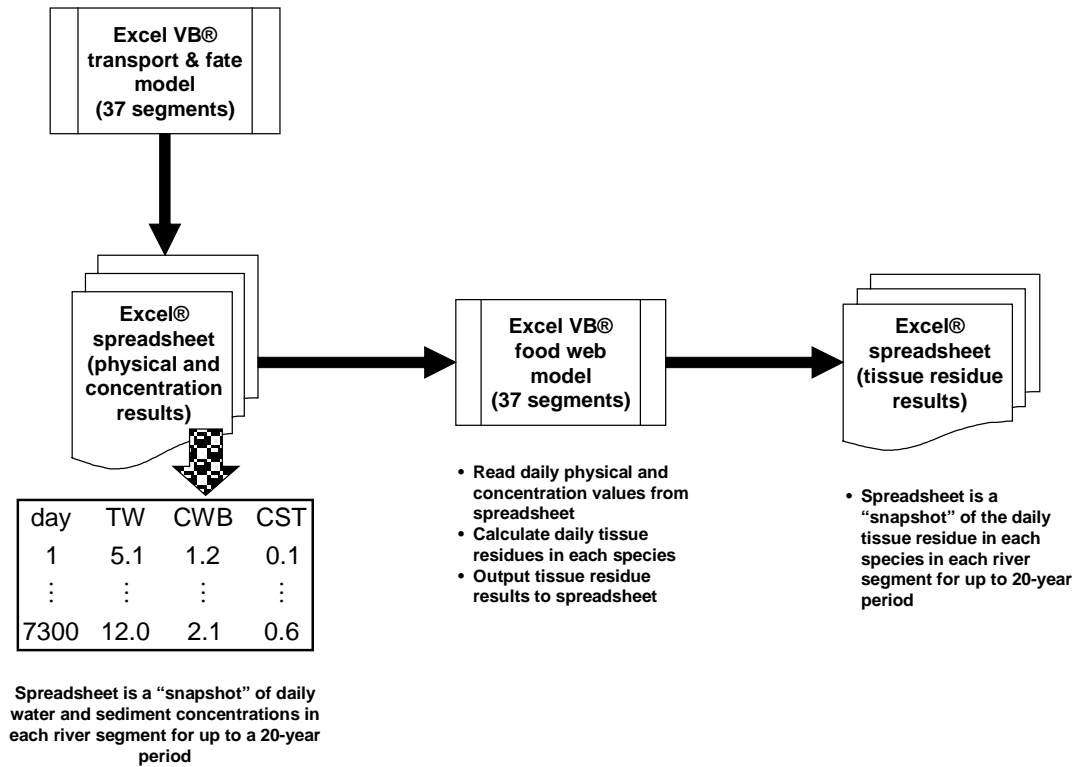
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FIGURE 1. Location of the Portland Harbor Superfund site within the Willamette Basin.



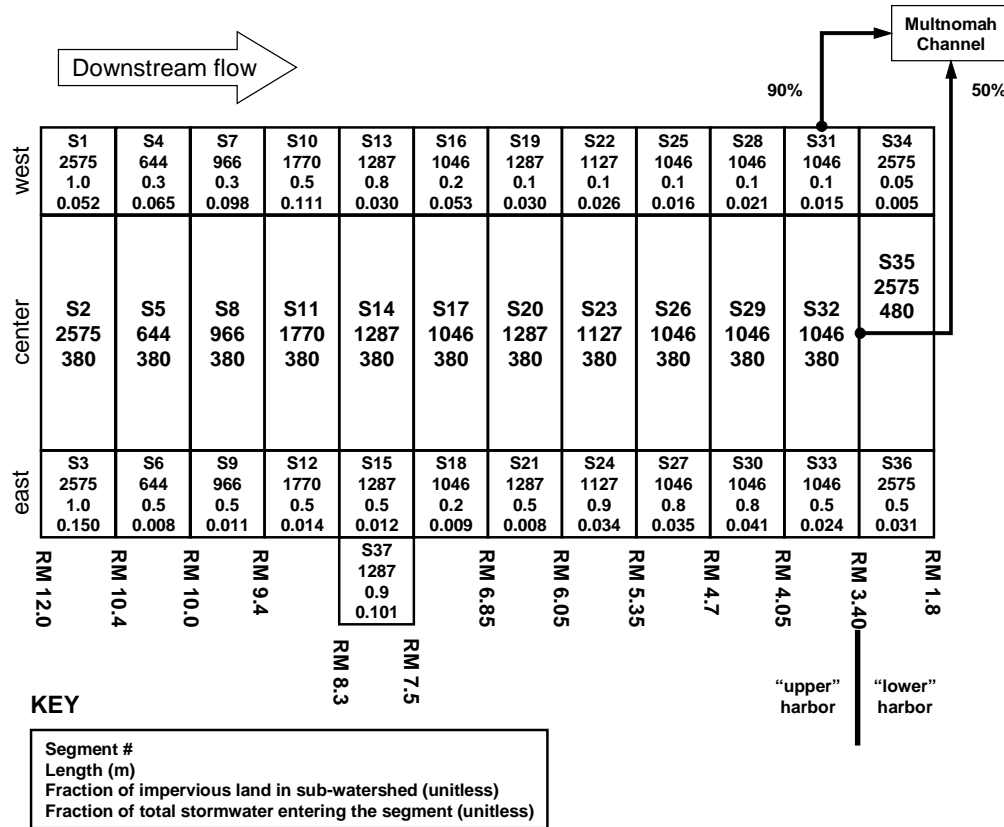
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FIGURE 2. Data linkages between the Harbor-specific transport and fate and food web models.



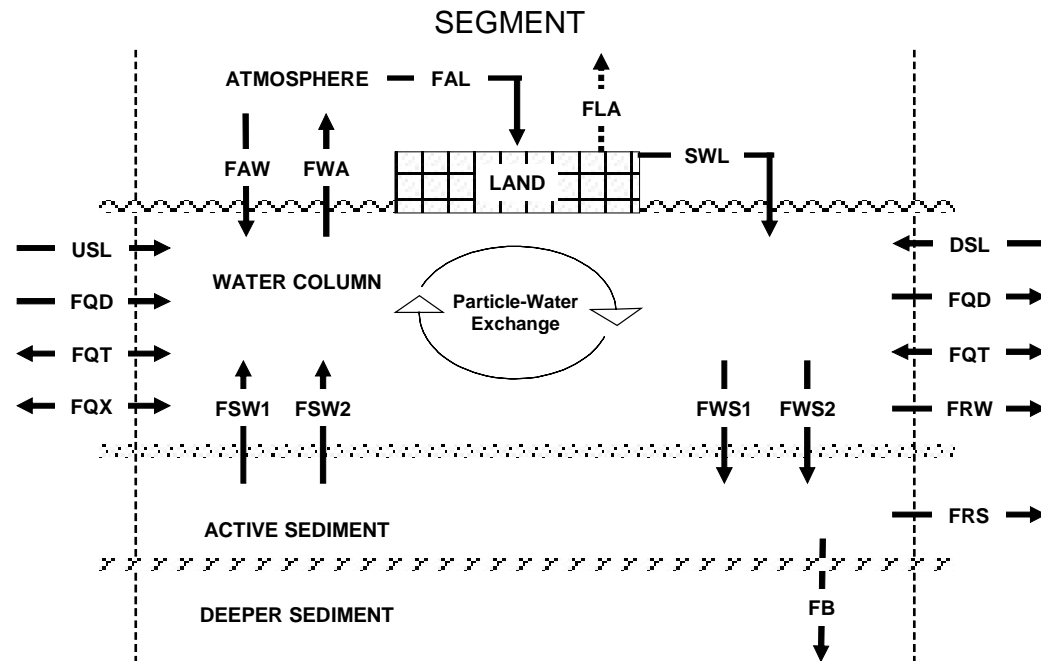
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FIGURE 3. Spatial arrangement and key physical dimensions of segments within the model domain.



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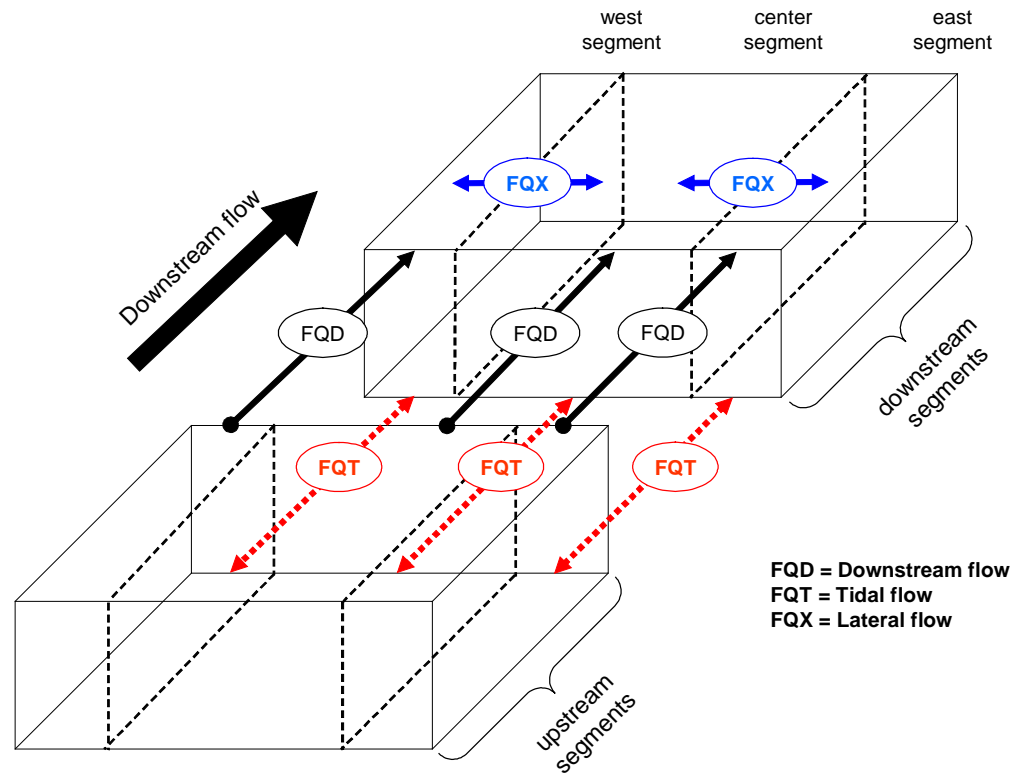
FIGURE 4. Chemical gain and loss fluxes within and between segments.



FQD = Downstream flow; FQT = Tidally-driven; FQX = Lateral; FWA = Volatilization from water; FLA = Volatilization from land; FAW = Air deposition to water; FAL = Air deposition to land; FRW = Degradation in water; FRS = Degradation in sediment; FB = Burial; FWS1 = Solids deposition; FWS2 = Water-to-sediment diffusion; FSW1 = Solids resuspension; FSW2 = Sediment-to-water diffusion; SWL = Stormwater load to water

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FIGURE 5. Schematic of flows between segments.



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FIGURE 6. Estimated seasonally-varying stormwater flows to the Harbor.

